# DISSIPATION OF MEVINPHOS FOLLOWING APPLICATION TO HEAD LETTUCE, LEAF LETTUCE, CAULIFLOWER, AND CHINESE CABBAGE

Ву

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### SUMMARY

In the spring and summer of 1984, a study was conducted in the Salinas Valley of California to evaluate the current 48-hour reentry interval required for mevinphos. Various vegetable crops, treated with mevinphos, were monitored to determine the decomposition rate of dislodgeable residues on foliage. Samples were collected periodically for three to four days. In general, this study supported earlier studies as mevinphos residues dissipated quite rapidly. One exception being two plots of Chinese cabbage in which the residues seemed to dissipate more slowly.

#### INTRODUCTION

Mevinphos (2-carbomethoxy-1-methyl-vinyl dimethyl phosphate, Phosdrin<sup>R</sup>), a highly toxic organophosphate insecticide, is registered for use on a number of vegetable and fruit crops in California. In 1983, there were 104,593 pounds of mevinphos (all isomers) reported as applied to head lettuce; 10,026 pounds applied to leaf lettuce; and, 21,512 pounds to cauliflower (1). Mevinphos consists of not less than 60 percent of the alpha (cis) isomer and 40 percent (or less) related compounds, including the beta (trans) isomer. The alpha isomer is about 100 times more toxic to insects and mammals than the beta isomer. The alpha isomer is also much less stable (2). Mevinphos (alpha isomer) has an oral LD50 (rat) of 3.7 - 6.1 mg/kg; a dermal LD50 of 4.2 - 4.7 mg/kg (3).

Since 1949, there have been a number of multiple case field worker poisoning incidents that occurred as a result of exposure to high levels of organophosphate residues and their breakdown products (4). The severity of these poisonings depends on a number of factors: 1) the toxicity of the pesticide applied; 2) the toxicity of the pesticide's degradation products; 3) the amount of the parent material and its breakdown products on the foliage (and the soil) at the time of exposure; and, 4) the duration and extent of contact with the residues. During this same time period, exposure to mevinphos residues (either alone or in combination with Metasystox-R or phosphamidon) has resulted in three field worker poisoning incidents (4). All three incidents were the result of workers entering a field prior to the expiration of the existing reentry interval.

In the early 1970's, the California Department of Food and Agriculture (CDFA) established reentry intervals in order to reduce the potential for excessive exposure of field workers to pesticide residues (5). Basically, these reentry itervals provide a period of time after pesticide application during which no unprotected persons may enter a field and come into contact with potentially hazardous residue levels. The current reentry interval for mevinphos is four days on citrus, grapes, nectarines, and peaches and 48 hours on all other crops. Many of the current reentry intervals were set in 1971 (with limited information) on the basis of reported illnesses, crops in which workers became ill, and time elapsed from application to onset of illness (6). This study was undertaken in the spring of 1984 to evaluate the current reentry interval for mevinphos as presently used on various row crops grown commercially in the Salinas Valley of California.

# MATERIALS AND METHODS

Pending mevinphos applications were determined with the assistance of the Monterey and Santa Cruz County Agricultural Commissioner's staffs. For each application mentioned, the Pest Control Operator (PCO) conducting the application was contacted as was the grower involved. The PCO's staff generally provided assistance in locating the specific application sites. All applications were done using standard ground rigs with boom sprayers. Table 1 describes the pertinent information concerning application rates.

TABLE 1 - Characteristics of Mevinphos Applications

| Crop               | Product Used   | Application Rate<br>(lbs A.I./Acre) | Dilution Rate<br>(Gal./Acre) | Other Chemicals<br>in Tank Mix  |
|--------------------|--|-------------------------------------|------------------------------|---|
| Lettuce<br>(Head)  | Phosdrin 4E<br>Emulsifiable<br>Concentrate<br>Insecticide<br>(#201-289 AA) | 0.5<br>(MLR* - 1.0)                 | 100                          | Permethrin,<br>Diazinon,<br>Manzeb,<br>Spreader-<br>Sticker           |
| Cauli-<br>flower   | SoilServ<br>Phosdrin 4E<br>(#6973-12 AA)                                   | 1.0<br>(MLR* - 1.0)                 | 60 - 80                      | Metasystox-R Permethrin, Phosphamidon and/or Spreader- Penetrant      |
| Chinese<br>Cabbage | SoilServ<br>Phosdrin 4E<br>(#6973-12 AA)                                   | 0.25<br>(MLR* - 0.25<br>from SLN)   | 60                           | Endosulfan<br>and Diazinon<br>or Methomyl,<br>Diazinon and<br>Manzate |
| Lettuce<br>(Leaf)  | SoilServ<br>Phosdrin 4E<br>(#6973-12 AA)                                   | 1.0<br>(MLR* - 1.0)                 | 60                           | Manzate,<br>Methomyl<br>Glycol-<br>Buffer                             |

\*Maximum Label Rate

Foliar samples were collected using the methods described by Gunther, et. al. (7) and Iwata, et. al. (8) and adapting them to row crops. Fields to be treated were divided into three areas. One sampling row was marked in each area of the field. Sixteen leaf punches (each 2.54 cm in diameter) were collected from each sampling row. One sample consisted of 48 leaf punches collected in a glass jar (a composite of punches from the three sampling rows); three replicate samples were collected at each sampling interval for the cauliflower fields, and two replicates for the remaining crops.

Since mevinphos dissipates rather rapidly, samples were generally collected at intervals of six to eight hours. Pre-application samples were collected in the same manner as the post-application samples to determine residue levels present prior to the monitored application. Once collected, the sample jars were sealed with aluminum foil, capped and stored on wet ice. Samples were delivered to a mobile laboratory stationed in Monterey County within one hour of collection. Residue extraction began as soon as samples were delivered to the lab.

Foliar dislodgeable mevinphos residues (alpha isomer only) were extracted from the leaf in a water/Sur-Ten solution. The water was then extracted with ethyl acetate. Solutions of a known volume were made and analyzed with standard gas-liquid chromatographic techniques.

#### RESULTS

Samples were collected from five fields of head lettuce (heads already forming); five fields of cauliflower (one very young and four close to banding); two fields of Chinese cabbage; and one field of leaf lettuce. The results are presented in the following tables (2-6) and figures (1-3). The results represent the average levels of the alpha isomer of composite samples collected from all fields of each specific crop plus 95% confidence intervals. Empirically, temperature differences appeared to have little affect on the residue levels found during the course of the study. The results for the head lettuce fields are presented in Table 2 and Figure 1. As can be seen, the highest mean value detected was about 0.65 micrograms/square centimeter (ug/cm²). As stated earlier, the alpha isomer degrades quite rapidly. Residues (alpha isomer only) are seen to drop below 0.1 ug/cm² between 12 and 18 hours. By 48 hours (the end of the mevinphos reentry interval), mean residues had dropped below 0.01 ug/cm².

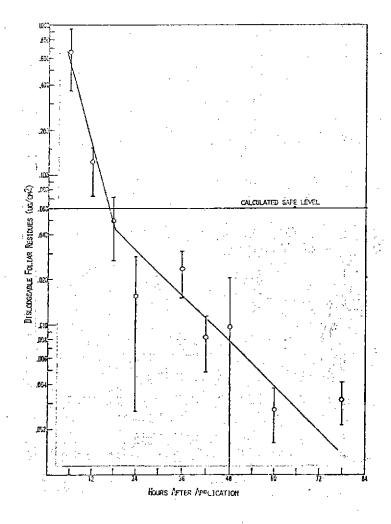


Figure 1: Mean foliar dislodgeable residues (alpha isomer) following application to head lettuce; the 95% confidence intervals are indicated.

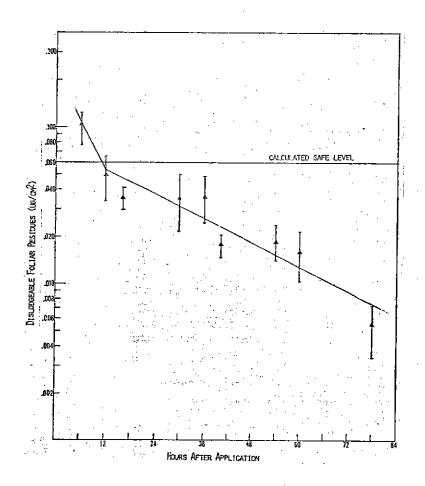


Figure 2: Mean foliar dislodgeable residues (alpha isomer) following application to cauliflower; the 95% confidence intervals are indicated.

TABLE 2: Mean Dislodgeable Residues
Alpha Isomer) on Foliage of Head
Lettuce (5 Fields)

| Mean Residue<br>(ug/cm <sup>2</sup> )(95% |
|---|
| <u>confidence interval)</u>               |
| ·   |
| 0.00003                                   |
| 0.658 <u>+</u> 0.295                      |
| $0.112 \pm 0.040$                         |
| $0.049 \pm 0.022$                         |
| $0.016 \pm 0.013$                         |
| $0.024 \pm 0.008$                         |
| $0.008 \pm 0.003$                         |
| $0.009 \pm 0.011$                         |
| 0.003 + 0.001                             |
| $0.003 \pm 0.001$                         |
|   |

Foliar dislodgeable residues found on the cauliflower foliage are shown in Table 3 and on Figure 2. As can be seen, the residue levels detected were very low. Some individual samples contained over  $0.06~\text{ug/cm}^2$  after 24 hours post-application (found at 30 and 36 hours). However, all fields had foliar residues below  $0.06~\text{ug/cm}^2$  within 48 hours. Surface residues (alpha isomer) found on the one very young cauliflower foliage were higher than those found on the foliage of the four other cauliflower fields (Table 4). (The results from this young field are also included in the results reported in Table 3 and on Figure 2.)

TABLE 3: Mean Dislodgeable Residues (Alpha Isomer) on Cauliflower Foliage (5 Fields)

TABLE 4: Mean Dislodgeable Residues (Alpha Isomer) on Young Cauliflower Foliage (One Field)

| Sample Interval | Mean Residue<br>(ug/cm <sup>2</sup> ) (95%<br>confidence interval) | Sample Interval) | Mean Residue (ug/cm²) |
|-----------------|--|------------------|-----------------------|
| Pre-Application | 0.0003   | Pre-Application  | ND*                   |
| 6 Hours         | 0.101 <u>+</u> 0.023   | 6 Hours          | 0.188                 |
| 12 Hours        | $0.050 \pm 0.016$  | 12 Hours         | 0.099                 |
| 16 Hours        | $0.035 \pm 0.006$  | 16 Hours         | 0.041                 |
| 30 Hours        | $0.036 \pm 0.014$  | 30 Hours         | 0.092                 |
| 36 Hours        | $0.036 \pm 0.012$  | 36 Hours         | 0.070                 |
| 40 Hours        | $0.018 \pm 0.003$  | 40 Hours         | 0.020                 |
| 54 Hours        | $0.019 \pm 0.005$  | 54 Hours         | 0.029                 |
| 60 Hours        | $0.016 \pm 0.006$  | 60 Hours         | 0.024                 |
| 78 Hours        | 0.006 + 0.002  | 78 Hours         | 0.008                 |

\*ND - None detected

Table 5 shows the mean foliar dislodgeable residues found on the two Chinese cabbage fields. Although only 0.25 pounds active ingredient (AI) were applied per acre, the mean residues seemed to dissipate more slowly. Field

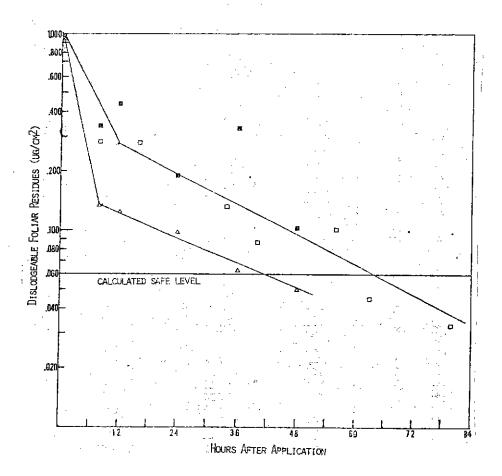


Figure 3: Mean foliar dislodgeable residues (alpha isomer) following application to Chinese cabbage (\_,) and leaf lettuce (\_).

1 had an average of  $0.103~\rm ug/cm^2$  at 48 hours, while Field 2 had an average of  $0.102~\rm ug/cm^2$  at 56 hours. The foliage on these plants seemed to be more dense and compact than either the lettuce or cauliflower sampled. Temperature does not appear to significantly affect the residue levels. Average temperatures found while sampling Field 1 were 64.5°F (max.) and 42.3°F (min.) while 73.8°F and 56.4°F were the average maximum and minimum temperatures found after the application to Field 2.

TABLE 5: Dislodgeable Residues
(Alpha Isomer) on Chinese Cabbage
(Two Fields)

| <u>Field 1</u>   |  |  | Field 2  |  |
|--|--|--|--|--|
| Sample Interval  | Mean Residue<br><u>(ug/cm<sup>2</sup>)</u>                   | Sample Interval  | Mean Residue<br>(ug/cm²)   |  |
| Pre-Application 1/2 Hour 8 Hours 12 Hours 24 Hours 36 Hours 48 Hours | 0.0001<br>0.966<br>0.338<br>0.440<br>0.189<br>0.331<br>0.104 | Pre-Application 8 Hours 16 Hours 32 Hours 40 Hours 56 Hours 63 Hours | Not Taken<br>0.283<br>0.280<br>0.132<br>0.087<br>0.102<br>0.045<br>0.033 |  |

Dislodgeable residue breakdown was also followed on one field of leaf lettuce (Table 6). As in most of the other fields, the residues dissipated quite rapidly; below  $0.06~\rm ug/cm^2$  prior to the expiration of the 48-hour reentry interval.

TABLE 6: Dislodgeable Residues (Alpha Isomer) on Leaf Lettuce (One Field)

| Sample Interval             | Mean Residue<br>(ug/cm²) |
|-----------------------------|--------------------------|
| Pre-Application<br>1/2 Hour | 0.0005<br>0.943          |
| 8 Hours                     | 0.134                    |
| 12 Hours 24 Hours           | 0.125<br>0.098           |
| 36 Hours                    | 0.063                    |
| 48 Hours                    | 0.050                    |

#### DISCUSSION

As noted by other investigators (2), mevinphos (alpha isomer) dissipates quite rapidly. The studies reported here support these previous findings. Analysis for other isomers (or decomposition products of mevinphos) was not conducted. The beta (trans) isomer is reported to be approximately 100 times less toxic than the alpha (cis) isomer. Thus, it would be unlikely that the beta isomer would significantly contribute to the toxic potential of the alpha isomer levels found in these studies.

It would appear that on lettuce and cauliflower foliage, mevinphos residues dissipate quite rapidly and by the expiration of the current 48-hour reentry interval, treated fields should pose little hazard to field workers. Knaak, et. al. (9) has calculated "safe levels" of dislodgeable residue for certain pesticides. The "safe level" for mevinphos has not been calculated by Knaak The safe level for parathion has been determined to be 0.09at this time.  $ug/cm^2$  (9). By setting up a ratio using the dermal LD<sub>50</sub> of mevinphos and parathion and the parathion safe level, a safe level can be calculated for mevinphos. This leads to a safe level of 0.06 ug/cm<sup>2</sup> for mevinphos. Using this safe level, the lettuce fields studied should have been safe for reentry at 48 hours (or before). Figure 1 indicates that under the conditions of this study, treated lettuce fields should pose little hazard for reentry between 12 and 18 hours after application. In looking at results from individual samples only, no composite lettuce samples had residues over 0.06  $ug/cm^2$  at 36 hours post-application. Figure 2 leads to a similar conclusion for mevinphos on cauliflower. Assuming 0.06 ug/cm<sup>2</sup> is the safe level for mevinphos, these fields could be safety reentered at 12 hours after application. No individual sample from the more mature fields (4 fields) were over 0.06 ug/cm<sup>2</sup> after 12 hours post-application. In one very young cauliflower field, the residues seemed to remain somewhat longer; a similar field should pose little hazard for reentry at 36 hours.

(Note: The residues found in this individual field (young cauliflower) exhibited an interesting characteristic that was seen in other fields sampled three times per day. Residue levels showed normal dissipation through a single day, but for each sample collected in the early morning, the levels found were much higher than the last sample collected the previous day. This may have implications on the timing of sample collection for reentry work since most field workers begin their workday at day break. This has also occurred with other pesticides.)

Figure 3 shows a slower decomposition rate for the alpha isomer on Chinese cabbage. Again, assuming the  $0.06~\rm ug/cm^2$  is the "safe level", it would be questionable if workers could have reentered that field safely at 48 hours. Four individual samples had levels higher than  $0.06~\rm ug/cm^2$  at the end of the reentry interval (1 at 48 hours; 3 at 56 hours after application). An empirical line of best-fit intersects  $0.06~\rm ug/cm^2$  at 63 hours post-application. Foliar residues seemed to dissipate more rapidly on leaf lettuce; with residues in this field reaching  $0.06~\rm ug/cm^2$  at 42 hours post-application.

# **CONCLUSIONS**

In general, it appears that under the conditions of these studies, a 48-hour reentry interval should be more than adequate to protect workers in most cases, with a possible exception being Chinese cabbage. More work needs to be completed before drawing conclusions on this crop.

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